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Calorimetric Study of the Order–Disorder Transformations in Graphite–Halogens

J. S. CULIK and D. D. L. CHUNG

Departments of Electrical Engineering and Metallurgy and Materials Science, Carnegie–Mellon University, Pittsburgh, Pa. 15213 (U.S.A.)

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SUMMARY

The first determination of the enthalpy and entropy of transformation for the order–disorder transformations in graphite intercalation compounds is reported here. By using differential scanning calorimetry, the order–disorder transformation associated with the intralayer intercalate position ordering has been observed at 375 ± 2 K in graphite–Br_2 and at 314 ± 2 K in graphite–ICl. The transformation temperatures show a strong dependence on the intercalate species but relatively little dependence on the intercalate concentration. The enthalpies of transformation are 108 ± 15 cal mol^{-1} bromine and 460 ± 50 cal mol^{-1} ICl for graphite–Br_2 and graphite–ICl respectively. Moreover, for graphite–Br_2 an endothermic peak at 277 ± 2 K has tentatively been identified with the order–disorder transformation associated with the intralayer intercalate molecular orientation ordering. The observed order–disorder transformations have all been found to be first-order transformations.

1. INTRODUCTION

The crystal structure of graphite intercalation compounds [1 - 5] involves two aspects: (1) the interlayer ordering (stacking order of the carbon and intercalate layers along the *c* direction) and (2) the intralayer ordering (arrangement of the intercalate ions, atoms or molecules within an intercalate layer).

1.1. Interlayer ordering

The interlayer ordering consists of two aspects: stage ordering and intercalate layer ordering.

The stage ordering is concerned with the ordering of the intercalate layers with respect to the carbon layers. In this type of ordering the carbon and intercalate layers are stacked in a periodic sequence such that the intercalate layers are separated by *n* contiguous graphite layers ($n > 1$), where *n* denotes the stage of the compound. As the intercalate concentration increases, *n* decreases. The stage ordering has been observed by means of X-ray diffraction in essentially all known graphite intercalation compounds.

The intercalate layer ordering is concerned with the ordering of the intercalate layers with respect to other intercalate layers. In the intercalate layer ordering, intercalate layers occupying different in-plane sites (*e.g.* α, β, γ, δ sites in C_8K [6]) are correlated with one another. Such a correlation of intercalate layers has been observed in a few compounds, *e.g.* C_8K [6 - 8], C_8Rb [8], C_8Cs [8], $C_{24}K$ [8], $C_{24}Rb$ [8], $C_{24}Cs$ [8], $C_{24}HSO_4 \cdot 2H_2SO_4$ [9] etc. For example, the first stage graphite–alkali metals C_8K and C_8Rb have the stacking sequence $A\alpha A\beta A\gamma A\delta A$ [6, 7], where A is a graphite layer and α, β, γ and δ are intercalate layers.

1.2. Intralayer ordering

The intralayer ordering also consists of two aspects: intralayer intercalate position ordering and intercalate molecular orientation ordering. The latter aspect applies only to compounds containing molecular intercalate species.

The intralayer intercalate position ordering is concerned with the ordering of the positions of the intercalate atoms, ions or molecules within an intercalate layer. The only compound in which the intralayer intercalate position ordering has been firmly established is C_8K [6, 7]. The intralayer structure is very complicated, particularly for molecular intercalation compounds such as graphite–Br_2 [10], graphite–ICl [11], graphite–$FeCl_3$ [12] and graphite–$MoCl_5$ [13]. In-plane unit cell dimensions are often of the order of 100 Å for molecular intercalation compounds [10, 11].

For molecular intercalates, in addition to the position ordering there is molecular orientation ordering which stems from the various orientations a molecule can assume with respect to the graphite lattice. Since graphite has a three-fold symmetry, an intercalate molecule can most probably assume three different orientations 120° apart on a layer plane. The molecular orientation ordering is associated with the alignment of the intercalate molecules and with the freezing of the various motions of the intercalate molecules.

1.3. Types of order–disorder transformations

The different types of ordering, as summarized in Table 1, promise an abundance of order–disorder transformations. We predict that the transformation temperatures follow the trend $T_S^{\rm inter} > T_P^{\rm intra} > T_I^{\rm inter} > T_0^{\rm intra}$. For temperatures $T > T_S^{\rm inter}$, the periodic stacking of the carbon and intercalate layers is lost and the only interlayer ordering remaining is the graphite AB stacking for the carbon layers. For temperatures $T_S^{\rm inter} > T > T_P^{\rm intra}$, two-dimensional stage ordering is present while there is no ordering within each intercalate layer. For temperatures $T_P^{\rm intra} > T > T_I^{\rm inter}$, the intercalate atoms, ions or molecules are ordered in definite sites on an intercalate layer, but the sites in different intercalate layers are not correlated. For temperatures $T_I^{\rm inter} > T > T_0^{\rm intra}$, three-dimensional ordering is present, but for the case of molecular intercalates the orientation of individual intercalate molecules is random. For temperatures $T < T_0^{\rm intra}$, the orientation of each intercalate molecule in its specific site is fixed.

TABLE 1

Types of ordering in graphite intercalation compounds

Type of ordering	Order–disorder transformation temperatures
Interlayer	
Stage ordering	$T_S^{\rm inter}$
Intercalate layer ordering	$T_I^{\rm inter}$
Intralayer	
Position ordering	$T_P^{\rm intra}$
Molecular orientation ordering[a]	$T_0^{\rm intra}$

[a] Only applies to molecular intercalates.

Although there are numerous types of order–disorder transformations in graphite intercalation compounds, relatively little is known concerning them. Most of the reported experimental observations of phase transformations in graphite intercalation compounds are concerned with the order–disorder transformation associated with the intralayer intercalate position ordering. Such observations have been made on compounds of a variety of intercalate species, *e.g.* bromine [14], ICl [14], IBr [14, HNO_3 [15 - 18], potassium [8, 14, 19, 20], rubidium [8, 14, 19, 20] and caesium [8, 14], 19 - 21]. Some experimental evidence has recently been reported on the phase transformations associated with the interlayer intercalate layer ordering in C_8Rb [22]. Order–disorder transformations associated with the intralayer molecular orientation ordering may be tentatively identified with some experimental observations [10, 17, 23]. No observation has yet been made of the order–disorder transformation associated with the interlayer stage ordering.

The first use of the differential scanning calorimetry (DSC) technique to study the order–disorder transformations in graphite intercalation compounds is reported here.

2. EXPERIMENTAL

2.1. Technique

The calorimetric study was performed by using a Perkin–Elmer DSC-1B differential scanning calorimeter, a block diagram of which is shown in Fig. 1. The calorimeter is programmed to vary the average temperature of the sample pan and the reference pan (typically empty) at a constant rate, such as 10 K $\min^{-1}$. Differential power is supplied to keep the temperature of the sample pan equal to that of the reference pan. As the average temperature changes the power supplied to the sample with respect to the reference is constant, except when the sample undergoes a phase transformation that involves latent heat. When this occurs, the power supplied to the sample changes with respect to that supplied to the reference and results in a maximum or a minimum at the transformation temperature on the strip-chart recorder trace.

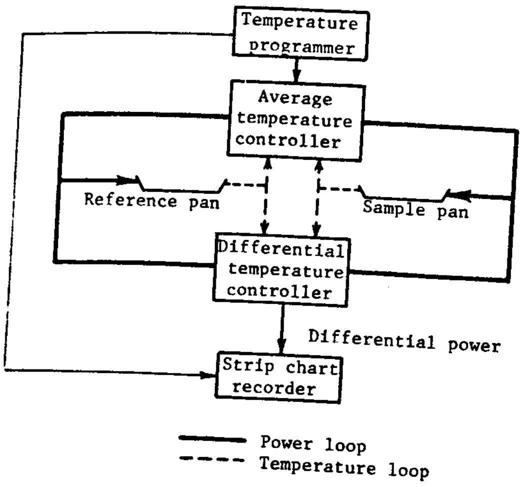


Fig. 1. A block diagram of the Perkin–Elmer DSC-1B differential scanning calorimeter.

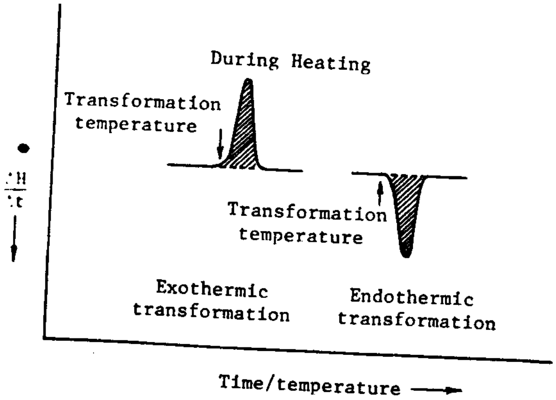


Fig. 2. DSC schematic recorder traces for exothermic and endothermic transformations occurring during heating. The transformation temperature (indicated by an arrow) is the temperature at which the trace first deviates from the baseline (indicated by a broken line) as the temperature increases or decreases. The shaded areas are directly related to the heats of the transformations.

Schematic recorder traces are shown in Fig. 2. The vertical axis corresponds to the differential power $\Delta H/\Delta t$, where H is enthalpy and t is time. By convention the $\Delta H/\Delta t$ scale increases in the direction from the top to the bottom of the plot. In this work a scale of 0.2 mcal s^{-1} per inch was used. The horizontal axis corresponds to time t, which is directly related to the temperature since the temperature is made to vary linearly with time. In this context, exothermic transformations give rise to local maxima in the recorder traces, whereas endothermic transformations give rise to local minima, as illustrated in Fig. 2. Order–disorder transformations are endothermic on heating (from order to disorder) and exothermic on cooling (from disorder to order). Thus, order–disorder transformations give rise to minima on heating and maxima on cooling. The transformation temperature is given by the temperature at which the trace first deviates from the baseline as the temperature increases or decreases, as illustrated in Fig. 2. Since the vertical axis corresponds to $\Delta H/\Delta t$ and the horizontal axis corresponds to t, the heat or enthalpy ΔH of a transformation is directly proportional to the area of the peak (shaded area in Fig. 2). In this work heat and temperature calibrations were performed by using the melting of indium.

The DSC experiment was carried out with the sample in a chamber purged with dry nitrogen gas. Before each scan, the sample was cooled to approximately 190 K and allowed to equilibrate for about 10 min. All scans were performed with the temperature changing at a constant rate ranging from 10 to 2.5 K min^{-1}.

2.2. Results

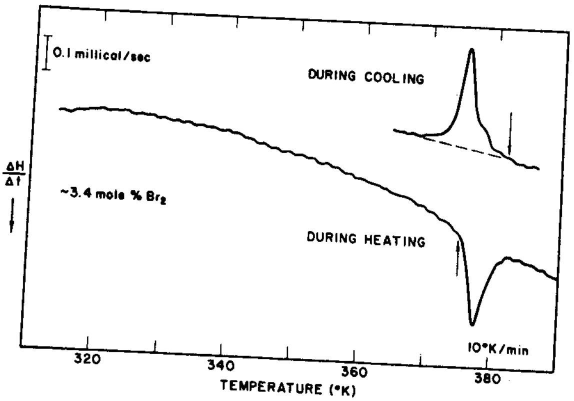


Fig. 3. High temperature DSC spectrum of a graphite–Br_2 lamellar compound (sample B-11) containing about 3.4 mol. % Br_2 obtained after 166 h of room temperature desorption from the saturated intercalate concentration.

Figure 3 shows the high temperature DSC spectrum of graphite–Br_2 (sample B-11) which was prepared by exposing pristine highly oriented pyrolytic graphite to bromine vapor at room temperature for about a week. This exposure resulted in a saturated second stage graphite–Br_2 lamellar compound (C_{16}-Br_2, *i.e.* 6.25 mol. % bromine). The recorder traces shown in Fig. 3 were taken after the sample had undergone 166 h of room temperature desorption. Gravimetric measurement showed that the partially desorbed lamellar compound contained about 3.4 mol. % bromine. As shown in Fig. 3, an endothermic transformation was observed at 375 K during heating. During cooling, the transformation was exothermic and occurred at 382 K. The anomalous hysteresis of this transformation is not understood at present.

Similar traces were obtained for graphite–Br_2 samples of various intercalate concentrations. A series of recorder traces are shown in Fig. 4 for graphite–Br_2 (sample B-8) after different periods of room temperature desorption: (i) after 69 h (about 4.0 mol. % bromine), (ii) after 165 h (about 3.4 mol. % bromine) and (iii) after 165 h and brief heating to 450 K (less than 3.4 mol. % bromine). Prior to the desorption process, the sample was a saturated second stage lamellar compound (6.25 mol. % bromine). The transformation shown in Fig. 3 was observed in the whole series of compounds (Fig. 4) at the *same* temperature. This shows that the transformation temperature is relatively insensitive to the intercalate concentration. In contrast, the peak area decreases significantly with decreasing intercalate concentration, indicating that the peak and the associated transformation are due to the intercalate.

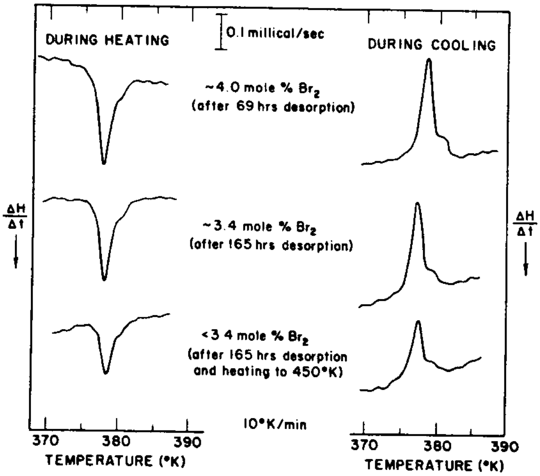


Fig. 4. DSC experimental recorder traces for the order–disorder transformation associated with the intralayer intercalate position ordering in graphite–Br_2 (sample B-8) of three different intercalate concentrations.

The transformation shown in Figs. 3 and 4 has been identified as the order–disorder transformation associated with the intralayer intercalate position ordering which was first observed at 379 ± 10 K by using electron diffraction [14]. The transformation temperature obtained from the DSC peak is within the experimental error of the electron diffraction result. However, the DSC technique provides a considerably more accurate determination of the transformation temperature than the electron diffraction technique since the DSC experimental uncertainty is ± 2 K. It is interesting to note that the order–disorder transformation temperature is much higher than the melting temperature of pure bromine (265.8 K). The enthalpy of this transformation has been determined for graphite–Br_2 of various intercalate concentrations, as shown in Table 2. It is relatively constant with intercalate concentration; the average value is [illegible] ± 15 cal (mol^{-1} Br_2). It should be noted that the enthalpy of the transformation is much smaller than that of the melting of pure bromine (2580 cal (mol^{-1} Br_2)).

The knee on the high temperature side of the peak, which is shown in Fig. 4, is of interest. This knee was observed during heating and cooling for all the graphite–Br_2 samples studied. The origin of this knee is not clear at present.

The DSC peak shown in Figs. 3 and 4 is only one observed in relatively dilute graphite–Br_2 in the temperature range 300 - 450 K. This peak was not observed in more concentrated samples since exfoliation was found to commence at temperatures as low as about 350 K for concentrated graphite–Br_2 compounds, which is below the order–disorder transformation temperature for the intralayer intercalate position ordering.

In addition to the 375 K peak, other peaks have been observed at low temperatures in graphite–Br_2. Figure 5 shows a series of low temperature DSC spectra observed in graphite–Br_2 (sample B-11) after different periods of room temperature desorption: (i) after 15 min (6.2 mol. % bromine), (ii) after 2 h (6.1 mol. % bromine) and (iii) after 23 h (4.9 mol. % bromine). Prior to the desorption process, the sample was a saturated second stage lamellar compound (6.25 mol. % bromine). In the first two traces shown in Fig. 5, three distinct endothermic peaks were observed during heat-

TABLE 2

Enthalpies of transformation for the order–disorder transformations in graphite–Br_2

Sample no.	Intercalate concentration (mol. % Br_2)	Enthalpy of transformation (cal mol^{-1})			
		266 K[a]	277 K	297 K	375 K
B-8	6.25	17 ± 2	105 ± 5	11 ± 2	–
	6.18	–[b]	88 ± 4	11 ± 2	–
	3.96	–	–	–	98 ± 5
	3.40	–	–	–	102 ± 5
B-11	6.25	24 ± 2	107 ± 5	–	–
	6.12	11 ± 1	93 ± 5	9.8 ± 1.5	–
	4.90	–	10.6 ± 0.5	–	–
	3.96	–	–	–	110 ± 6
	3.40	–	–	–	123 ± 6

[a] Enthalpies are calculated by assuming that the peak is due to intercalated rather than adsorbed bromine.
[b] Not observed.

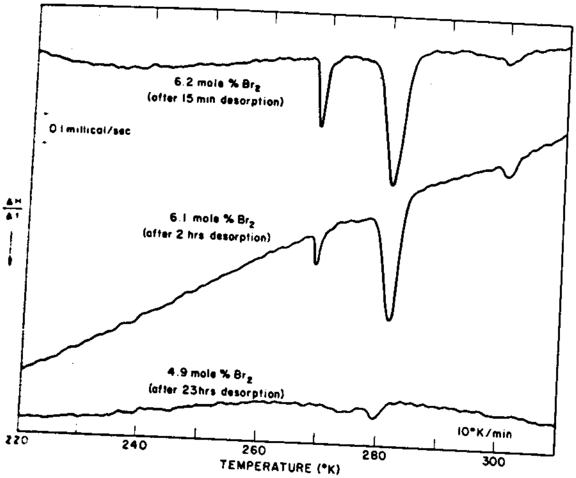


Fig. 5. Low temperature DSC spectra of graphite–Br_2 lamellar compounds (sample B-11) of three different intercalate concentrations. The traces shown were taken during heating.

ing. The first peak occurs at 266 K, which is the melting temperature of pure bromine, and the second peak occurs at 277 K. Both the first and the second peaks were observed during heating only. The third peak occurs at 297 K during heating and at 294 K during cooling. The transformation temperatures of all three peaks are relatively insensitive to the intercalate concentration, but their areas decrease significantly with decreasing intercalate concentration.

The top two spectra shown in Fig. 5 were obtained with no prior heating of the sample above room temperature. On a similarly prepared graphite–Br_2 sample, the DSC spectrum was first obtained at low temperatures. The sample was then briefly heated to 340 K, cooled and allowed to desorb at room temperature for about 1 h. After that, the low temperature DSC spectrum was again measured. In the DSC spectrum obtained after the heating process the first peak was absent, whereas the other two peaks were relatively unchanged. Thus, the first peak could be easily removed by heating. This observation, together with the fact that the first peak occurs exactly at the melting temperature of pure bromine, strongly suggests that this first peak (at 266 K) is due to the melting of the unintercalated bromine adsorbed onto the surface of the sample. This interpretation is further supported by the dependence of the enthalpy of the transformation on the intercalate concentration, as shown in Table 2, where the enthalpies of the transformation were calculated by assuming that intercalated rather than adsorbed bromine was responsible for the 266 K peak. Under this assumption, the enthalpy of the transformation per mole of bromine was found to decrease with decreasing intercalate concentration. Such a decrease would be expected if adsorbed bromine, which is quite unrelated to the intercalate concentration, were responsible for the transformation.

The second peak (at 277 K) in Fig. 5 is the dominant peak in the DSC spectrum of graphite–Br_2 between liquid nitrogen temperature and room temperature. For relatively dilute graphite–Br_2, this peak is the only observable one in this temperature range. In the same temperature range an intralayer crystal structural change has been observed by means of electron diffraction through the (001) plane of graphite–Br_2 [10, 23]. This structural change was detected as a change from streaks in the electron diffraction pattern at room temperature to closely spaced spots in the diffraction pattern at liquid nitrogen temperature. This effect is probably due to the order–disorder transformation associated with the intralayer molecular orientation ordering [23]. Since this is the dominant structural change observed in graphite–Br_2 between liquid nitrogen temperature and room temperature and furthermore since this was observed in electron diffraction specimens which are necessarily partially desorbed, the correspondence between this structural change and the 277 K DSC peak is highly probable. Therefore we tentatively identify the 277 K DSC peak with the order–disorder transformation associated with the intralayer intercalate molecular orientation ordering. The fact that this 277 K DSC peak was only observed during heating suggests that this transformation exhibits a great deal of hysteresis. The enthalpy of this transformation has been determined for graphite–Br_2 of various intercalate concentrations, as shown in Table 2. It ranges from 10.6 to 107 cal mol^{-1} Br_2, decreasing significantly with decreasing intercalate concentration. This behavior may be due to the interlayer intercalate interaction which becomes more important as the temperature decreases and as the degree of interlayer intercalate layer ordering increases. As the intercalate concentration increases, the spacing between the nearest intercalate layers decreases. This results in a stronger interlayer interaction, which increases the stability of the molecular orientation ordering. Thus the inthalpy of the transformation increases with increasing intercalate concentration.

Since the order–disorder transformation temperature for the intercalate layer ordering is expected to be higher than that for the interlayer intercalate molecular orientation ordering, the peak at 297 K may be due to the order–disorder transformation associated with the interlayer intercalate layer ordering. However, it should be emphasized that this interpretation is highly tentative. Detailed diffraction work around this temperature is necessary to investigate the structural change which accompanies the observed heat change. The enthalpy of this transformation has been determined for graphite–Br_2 of various intercalate concentrations, as shown in Table 2. The average value is 10.5 ± 0.6 cal mol^{-1} Br_2.

Figure 6 shows a series of DSC recorder traces for graphite–ICl after different periods of room temperature desorption: (i) after 21 min (9.35 mol. % ICl) and 24 min (9.32 mol. % ICl); (ii) after 185 min (8.48 mol. % ICl) and 189 min (8.47 mol. % ICl); (iii) after 193 min (8.46 mol. % ICl) and 196 min (8.45 mol. % ICl); (iv) after 214 min (8.39 mol. % ICl) and 211 min (8.40 mol. % ICl); (v) after eight days (4.48 mol. % ICl). Prior to the desorption process, the sample was a saturated lamellar compound (about 11.7 mol. % ICl), which was prepared by exposing pristine highly oriented pyrolytic graphite to ICl vapor at room temperature for five days. Even at the highest intercalate concentration, only two peaks

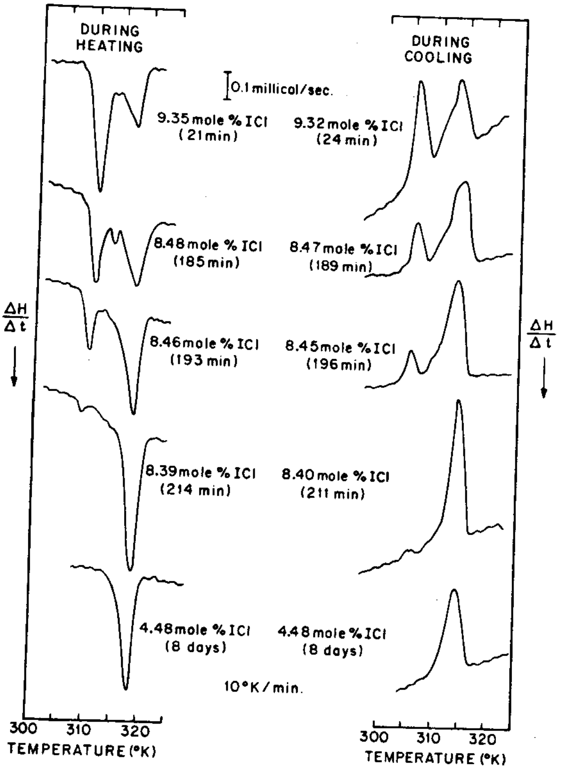


Fig. 6. DSC experimental recorder traces of graphite–ICl of different intercalate concentrations which were obtained after different periods of room temperature desorption of the same sample. The desorption time for each trace is shown in parentheses.

TABLE 3

Thermodynamic properties associated with the intralayer intercalate position order–disorder transformations in graphite–halogens

	T_c[a] (K)	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
Graphite–Br_2	375	210	0.56
Bromine[b]	265.8	2580	9.74
Graphite–ICl	314	460	1.45
K–ICl[b]	300.2	2660	8.86

[a] Observed during heating.

[b] The thermodynamic properties given are for the melting of the pure intercalate.

were observed in the temperature range 190 - 325 K. As with graphite–Br_2, the transformation temperatures are relatively insensitive to the intercalate concentration but the areas of both peaks depend strongly on the intercalate concentration. The transformation temperature for the lower temperature peak is 308 K during heating. Because of the method of obtaining transformation temperatures from DSC peaks (as illustrated by the arrows in Fig. 2), the transformation temperature for the higher temperature peak during heating can most accurately be obtained from the bottom DSC trace which shows a relatively clear onset of the higher temperature peak during heating owing to the small height of the lower temperature peak in this trace. The transformation temperature thus obtained for the higher temperature peak during heating is 314 K. Similar behavior was observed during cooling.

The area of the lower temperature peak shown in Fig. 6 decreases with decreasing intercalate concentration. However, the area of the higher temperature peak at first increases and then decreases with decreasing intercalate concentration. Since only the higher temperature peak was observed in dilute graphite–ICl, this peak has tentatively been identified with the order–disorder transformation associated with the intralayer intercalate position ordering. This identification is supported by the electron diffraction observation of this transformation in dilute graphite–ICl at 316 ± 10 K [14]. The lower temperature peak may correspond to another type of order–disorder transformation in graphite–ICl.

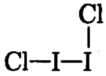
The enthalpy of the 314 K peak has been determined to be 460 ± 50 cal mol^{-1} ICl for a graphite–ICl compound containing 4.33 mol % ICl. The sample was a partially desorbed lamellar compound which had undergone nine days of room temperature desorption after attaining the saturated intercalate concentration. The enthalpy of the transformation is much smaller than that of the melting of pure ICl (2660 cal mol^{-1} ICl). In contrast, the enthalpy of the 308 K peak has been determined to be of the order of 300 cal mol^{-1} ICl during the first 3 h of room temperature desorption.

3. DISCUSSION

The thermodynamic properties associated with the intralayer intercalate position order–disorder transformations in graphite–Br_2 and graphite–ICl are shown in Table 3 where these properties are compared with corresponding ones for the melting of the pure intercalates. The transformation temperatures T_c and the enthalpies of transformation ΔH were determined experimentally; the entropies of transformation ΔS were calculated by using the relation

$$\Delta S = \frac{\Delta H}{T_c}$$

The transformation temperatures for the intralayer intercalate position order–disorder transformations are considerably higher than the melting temperatures of the corresponding pure intercalates. This indicates that intercalate–intercalate interaction alone does not account for the ordering of the intercalate molecules in the graphite lattice. Furthermore, the transformation temperatures vary strongly with the intercalate species but show relatively little dependence on the intercalate concentration. This is consistent with the fact that the intralayer intercalate crystal structure of the graphite–halogens depends strongly on the intercalate species but is relatively independent of the intercalate concentration [14]. The transformation temperature is higher for graphite–Br_2 than for graphite–ICl, in spite of the fact that the melting temperature of pure bromine is lower than that of pure ICl. This behavior may be explained by considering the geometrical factor. Bromine is a molecular solid consisting of symmetrical Br—Br molecules which are arranged in layers with the molecular axes on the plane. In solid ICl, however, I—Cl molecules are associated in pairs of the form



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl—I—I} \end{array}$$

so that each dimer partly lies on the plane and partly protrudes out of the plane at roughly right angles [24]. Similar situations probably exist for the intercalated bromine and ICl. Owing to the bulkiness and the asymmetry of the $(ICl)_2$ dimers, it is geometrically simpler to order bromine molecules than ICl molecules in the graphite interlayer space. Therefore, a lower temperature is necessary for ordering to occur in graphite–ICl than in graphite–Br_2.

The enthalpies of the intralayer intercalate position order–disorder transformations are much lower than those for the melting of the corresponding pure intercalates. This means that the internal energy difference between the ordered and disordered states of the compound is much smaller than the internal energy difference between the solid and liquid states of the pure intercalate. Furthermore, the enthalpy of transformation varies with the intercalate species but shows relatively little dependence on the intercalate concentrations. As shown in Table 3, the enthalpy of the intralayer intercalate position order–disorder transformation in graphite–ICl is much higher than that in graphite–Br_2. This can be explained by considering the bulkiness and the asymmetry of the $(ICl)_2$ dimers which require more energy for motion.

The entropies of the intralayer intercalate position order–disorder transformations are much lower than those for the melting of the corresponding pure intercalates. This suggests that (i) the degree of in-plane order in compounds with intralayer intercalate position ordering is lower than that in pure intercalate solids, owing to the imperfect intercalate molecular orientation ordering in the former, and (ii) the degree of in-plane order in compounds without intralayer intercalate position ordering is higher than that in pure intercalate liquids, owing to the influence of the graphite template on the former. Furthermore, the entropy of transformation varies with the intercalate species but shows relatively little dependence on the intercalate concentration. As shown in Table 3, the entropy of the intralayer intercalate position order–disorder transformation in graphite–ICl is much higher than that in graphite–Br_2.

An important implication of our observation of latent heats for the various order–disorder transformations is that all of the observed transformations are first order transformations. Our conclusion is in contrast to the assumption that the order–disorder transformation in graphite nitrate at —20 °C is of the λ type [15 - 18].

In summary, this work has provided the first determination of the enthalpy and entropy of transformation for the order–disorder transformations in graphite intercalation compounds. The order–disorder transformation associated with the intralayer intercalate position ordering in the graphite–halogens, which has previously been observed by using electron diffraction [14], has been confirmed. Additional peaks in the DSC spectra have been tentatively identified with order–disorder transformations associated with the intercalate molecular orientation ordering and with the interlayer intercalate layer ordering.

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